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Growth of Nickel Sulfate in a Laboratory-Scale Fluidized-Bed Crystallizer

Growth and dissolution rates of nickel sulfate α-hexahydrate were measured as functions of the concentration driving force in a laboratory-scale fluidized-bed crystallizer for the temperature range 35° to 50°C and the crystal size range 0.5 to 4.0 mm.

Dissolution rates at a given temperature and crystal size were first order in the concentration driving force. Growth rates were about one-quarter of dissolution rates and depended on a higher exponent (around 1.3) of the concentration driving force. This exponent was not significantly affected by variations in crystal size, but decreased as temperature increased. The apparent variation of growth rate itself with crystal size at constant temperature was slight. Growth rates were found to be insensitive to solids concentration.

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SCOPE

Laboratory-scale studies of fluidized-bed crystallization are of interest as aids to the design of full-scale crystallizers of the suspended-bed (Krystal) type. Measurements on crystal growth rates under conditions simulating those in industrial crystallizers, especially Krystal crystallizers, are still relatively scarce. Crystal growth rates determined under controlled conditions can also be used to test theories of the mechanism of crystallization. In this respect, dissolution rates determined under comparable conditions indicate the role of mass transfer in the overall growth process.

The α-hexahydrate crystallizes from solution at temperatures between 31.2° and 53.3°C. Although nickel sulfate has some commercial significance (being a byproduct of copper refining and being used mainly in electroplating, in the preparation of catalysts and as a fungicide), no previous measurements could be found on the rates of growth of any of its hydrates. In the present work, growth and dissolution rates of the α-hexahydrate were measured as functions of the concentration driving force in a laboratory-scale fluidized-bed crystallizer. The range of temperature studied (with a constant crystal size of 1 mm) was 35° to 50°C and the range of crystal size studied (with a constant temperature of 40°C) was 0.5 to 4.0 mm.

The apparatus is shown in Figure 1. Supersaturated solution at constant temperature is continuously circulated around a vertical rectangular circuit. The circulation rate and the concentration of the solution are known. In the Differential Method (for which the void fraction is about 0.998), a series of separate experiments is made at each temperature and crystal size, the supersaturation or undersaturation level being almost constant within each experiment but different between experiments. A small weight of seed crystals is used and the growth or dissolution rate is found via the change in weight of the crystals. In the Integral Method (for which the void fraction is about 0.80, close to industrial levels), supersaturation or undersaturation levels are permitted to fall by a large amount while being continuously monitored. A large weight of seed crystals is used and growth or dissolution rates are found from the rates of fall-off of solution supersaturation or undersaturation. This method allows growth or dissolution rates to be determined much more rapidly, but its use for growth studies is restricted to low supersaturations. In the present work this method was applied only to the growth of 1 mm crystals at 40°C.

These are believed to be the first growth rate measurements reported for nickel sulfate, a compound of some commercial significance. While it is realized that in the industrial crystallization of nickel sulfate, the feed solutions are not pure, it is suggested that the present measurements represent the asymptotic growth rates as impurity levels tend to zero.

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CONCLUSIONS AND SIGNIFICANCE

Dissolution rates at a given temperature and crystal size (Figures 8 and 9) were first order in the undersaturation ($c^* - c$). Growth rates (Figures 4 and 5) were about one-quarter of dissolution rates and depended on a higher exponent (around 1.3) of the supersaturation ($c - c^*$). This exponent was not significantly affected by variations in crystal size but decreased as temperature increased (from 1.39 at 35°C to 1.16 at 50°C). Of the rates themselves, the dissolution rate was affected much less by temperature than was the growth rate. Both dissolution rate and growth rate increased only slowly with crystal size. The absolute values of the growth and dissolution rates were comparable to those published for other simple inorganic salts: for example, at a supersaturation of 1 wt. % hexahydrate, the growth rate at 40°C was about 15 $\times$ 10^{-5} kg/m^2 · s while at an undersaturation of 1 wt. % hexahydrate, the dissolution rate at 40°C was about 50 $\times$ 10^{-5} kg/m^2 · s.

In the supersaturation range 0.0 to 0.7 wt. % hexahydrate, which includes the usual industrial levels, results from the Integral Method agreed well with those from the Differential Method, despite different void fractions in the two methods. This agreement reinforces and extends to lower void fractions similar findings by earlier workers. Earlier workers also found agreement between growth rates from the Differential Method and from single crystal tests, so the strong implication is that only single crystal tests need be made to predict the growth rate prevailing in an industrial-type fluidized bed. This would considerably simplify the problem of crystallizer design.

On the theoretical side, the nature of the dependence of the growth rate on temperature and on crystal size supports the general concept of crystallization as a two-step process, that is, mass transfer of solute to the crystal surface, followed by integration into the solid lattice. In the present case, the growth rate appears to be mainly but not wholly controlled by the surface integration step. Making the assumption that the (unknown) rate constant for the mass transfer step of growth can be represented by the (known) rate constant for dissolution, the apparent kinetics of the surface integration step of growth have been extracted from the overall kinetics of growth.

BRIEF REVIEW OF PREVIOUS WORK

While there are many crystal growth rate measurements in the literature, most are not in a form useful for crystallizer design. It is only in the last ten years or so that measurements have been made of growth rates under conditions approximating those in industrial crystallizers. The population balance technique (Randolph and Larson, 1971) has been fruitful in the case of continuous stirred-tank crystallizers but for fluidized-bed type (Krystal) crystallizers, growth rate measurements are still relatively scarce. Few studies have compared the two types of crystallizer (Ishii ,1965; Bujac, 1969).

In an early study, Rumford and Bain (1960) investigated the possibility of using a fluidized bed for growing large sodium chloride crystals industrially. They examined the effect of temperature on growth rate and on the mechanism controlling growth, finding mass transfer control above 50°C. Mullin and Garside (1967) grew potassium alum both as single crystals and in lean fluidized beds at a constant void fraction of around 0.95, investigating the effects of temperature and crystal size on the growth rate. When adjusted to equivalent solution slip velocities, the growth rates for single crystals and for crystals in lean fluidized beds were in good agreement. Growth rates of potassium sulfate in lean fluidized beds were measured by Rosen and Hulburt (1971) and by Mullin and Gaska (1969). Both pairs of workers investigated the effects of solution velocity and of crystal size and the latter pair also investigated the effect of temperature. In general the findings of the two pairs of workers were consistent. Also Graeser (1972) has investigated the effect of temperature and of surfactants on the growth of potassium sulfate. In a later paper (1973), Mullin and Gaska compared their growth rates from lean fluidized beds with single crystal growth rates. Bujac and Mullin (1969) grew ammonium alum in both lean fluidized beds (void fraction around 0.95) and in more dense fluidized beds (void fraction around 0.90), finding agreement between growth rates in the two cases. Garside et al. (1972) also compared growth rates from lean and dense beds.

In the final section of the present paper, the apparent kinetics of the surface integration step of growth have been extracted from the overall kinetics of growth by making the assumption that the mass transfer step of growth under given hydrodynamic conditions can be represented by dissolution rate expressions obtained from experiments on dissolution rates under the same hydrodynamic conditions. Although previous workers (for example, Hixson and Knox, 1951) had estimated the effect of the mass transfer step on growth simply by calculation using existing general mass transfer correlations, Tanimoto et al. (1964) were the first workers to use the more direct technique via dissolution experiments complementary to their growth experiments. While they only used this direct technique on stirred-tank crystallization, Ishii (1965, 1973) later used it on crystallization in a conical fluidized bed as well. Mullin and Garside (1968) have used the technique in their fluidized bed study of potassium alum crystallization, but they warn of physical considerations which undermine the assumption that dissolution expressions are applicable to the mass transfer step of growth.

LABORATORY-SCALE FLUIDIZED-BED CRYSTALLIZER

The crystallizer (Figure 1), mainly of glass, was a slightly modified version of that reported by Mullin and Garside (1967). Full details of the version used in the present work are available elsewhere (Phillips, 1973). Only an outline of the main modifications will be given here. One was the replacement of the original three-way crystal removal valve by a plain tee piece with a straight-through crystal removal valve below it. By keeping it immersed in a thermostatic water jacket except briefly when in use, one could operate this valve without grease, thereby

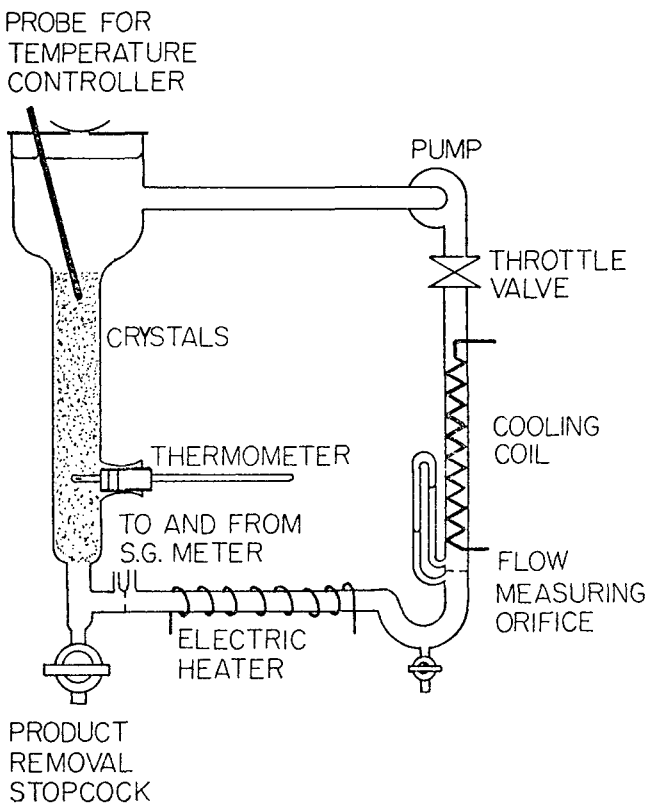

Fig. 1. The laboratory-scale fluidized-bed crystallizer.

eliminating a possible contaminant. Again to eliminate contamination of the solution, all tubing connections and gaskets were of Teflon. The relatively high viscosity of near-saturated nickel sulfate solutions (Phillips, 1972) meant that the solution circulation rates necessary to fluidize the crystal bed were small, and under these conditions the temperature differences between the ends of the uninsulated crystallization section were unacceptably high. Therefore, this section was fitted with a clear acrylic jacket, through which was pumped water at a temperature within 0.2°C of the temperature of the experiment. With the jacket fitted, the temperature difference fell to not more than 0.05°C. The various errors on the steady state temperature in the crystallization section, as measured by the main thermometer, were as follows: The calibration error of the thermometer was not more than 0.03°C. The mean temperature given by the thermometer never differed from the reported set temperature by more than 0.05°C. The half-wave amplitude of the sinusoidal variations in the instantaneous temperature, caused by the temperature control system, was never more than 0.07°C.

PREPARATION OF SEED CRYSTALS

The properties of the seed crystals are important in any experiments on crystal growth and this is particularly true of the present type of experiment in which the increase of crystal size during a growth experiment was only about 20% of the size of the seed crystals. Thus the average crystal shape and hence the average crystal surface area during an experiment were largely defined by the shape of the seed crystals. Also, the surface characteristics of the seed crystals (dislocation density, etc.), which may themselves have been governed by the conditions under which the seed crystals were grown, may influence any growth which is subsequently added to that surface.

It follows then that the seed crystals should be prepared under known, highly controlled conditions. In the present work the seed crystals were grown in the crystallizer from small starting crystals carefully selected from among those received from the manufacturer. Standard conditions were used for all these seed crystal preparation runs. All runs were made at 40°C with an initial supersaturation of 1.34 wt. % hexahydrate. A limit of 25% of this initial value was set on the permissible fall-off of supersaturation so that all the growth would occur not only at the same temperature but also at similar supersaturation levels and hence at similar rates, thus hopefully producing final surfaces having similar microscopic characteristics. To produce the large seed crystals, several successive growth stages were needed.

In the calculation of the overall crystal surface area, a regular crystal shape is assumed. In practice, about 30 wt. % of the seed crystals were found to show significant irregularities of shape, usually twinning. In absolute terms, the irregularities were not great (Figure 2) and no method could therefore be found for the easy separation of the regular from the irregular crystals. To estimate the effects of these irregularities on the growth rate, a few experiments were made by the Differential Method on 100% regular crystals, separated by hand sorting under a magnifier. Growth rates calculated from these experiments never differed by more than 2% from the rates calculated when using the normal seeds with 30 wt% irregular crystals.

EXPERIMENTAL METHODS

Solutions were prepared from nickel sulfate which met American Chemical Society specifications (Reagent Grade, J. T. Baker Co.) and from water distilled in glass. The solutions were preheated and then filtered through a 38 μm stainless steel screen as they were poured into the crystallizer. Between experiments the solutions were circulated in the crystallizer at

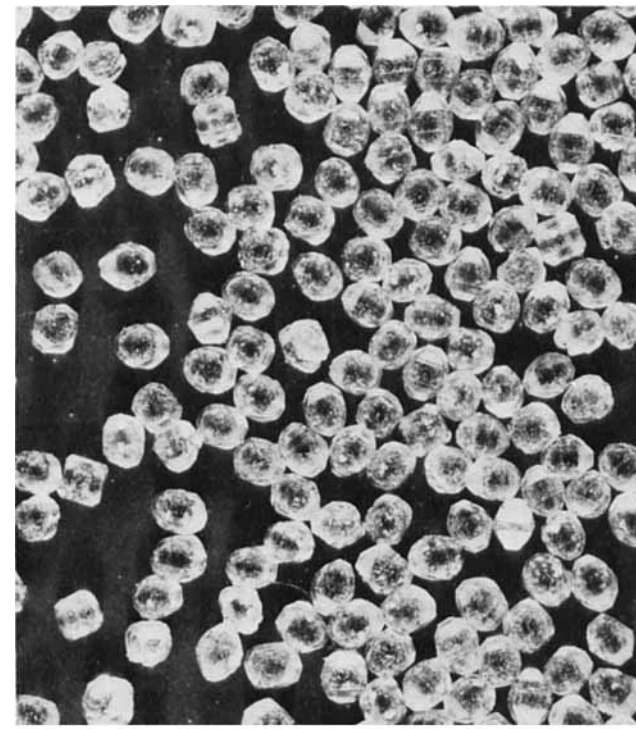

Fig. 2. Typical seed crystals (reflected light; life size 0.85-1.00 mm).

temperatures well above their saturation temperatures.

At the beginning of an experiment, the solution concentration was first adjusted to the desired value by suitable additions of stock solutions, the concentration being measured via its specific gravity (Phillips, 1972). The solution was then cooled to the desired temperature.

The Differential Method, described next, was based on the method reported by Mullin and Garside (1967). More details of both the Differential Method and the Integral Method (described later) are available elsewhere (Phillips, 1973). An accurately known weight (about 5 g. in the case of growth) of seed crystals (Figure 2), all within one size interval in the full U.S.A. Standard Sieve Series, was preheated and was then charged into the crystallizer. During charging, the solution circulation was briefly stopped, then restarted and adjusted to fluidize the crystals evenly throughout the 50-mm I.D. crystallization section, giving a mean void fraction of 0.998 during all experiments by the Differential Method.

Growth was continued until the total weight of crystals was about 9 g. This amount of growth was approximately equivalent to an increase in size from one interval to the next larger in the full U.S.A. Standard Sieve Series, a size increase of about 20%. As the crystals grew, the solution circulation rate had to be increased slightly (by about 15%) to maintain uniform distribution of the crystals within the crystallization section. The reported solution velocity was the arithmetic average of the initial and final values. The maximum permissible fall-off of supersaturation was set at 15% of the starting supersaturation, and again the reported supersaturation was the arithmetic average. The actual fall-off approached the maximum permissible at very low supersaturations because the starting supersaturations were then themselves low, and at high supersaturations because of nucleation (which began to be observed at supersaturations above about 1.3 wt. % hexahydrate).

When sufficient growth had occurred, solution circulation was stopped and after the crystals had settled to the product removal valve they were withdrawn and the accompanying solution was filtered off, with vacuum, in a sintered glass funnel. The crystals were then immediately given a washing with methanol, followed by a benzene rinse and finally slow air drying. Later their size distribution was determined by sieving. The procedure for dissolution experiments was the same as for growth, except that 9 g. of seeds were dissolved to 5 g. of product crystals.

A check was made that product crystal recovery was quantitative by settling preheated crystals through an accurately saturated solution and immediately withdrawing and washing them. The weights of crystals charged and recovered never differed by more than 0.025 g. Because the growth or dissolution rates during charging and withdrawing the crystals were different from the steady state rates, end correction measurements were made by means of dummy runs, in which crystals were settled through stagnant solutions of various supersaturations or undersaturations and then immediately removed for the usual filtration and washing processes.

In order to convert the measured weight change occurring in a known time into a crystal growth or dissolution rate in a conventional form (as a mass flux), an average overall crystal surface area was also needed. This was found from the size and weight of the crystals and from the overall surface-volume shape factor, the latter being determined as follows. Nickel sulfate α-hexahydrate crystals have a simple combination tetragonal bipyramidal shape (Figure 3) and, as discussed above, the seed crystals used in this work were mostly regular (Figure 2). Therefore average values of the linear parameters of the crystal shape (Figure 3) were found from microscopic measurements of 100 regular crystals for each of the crystal sizes used, and the overall surface-volume shape factor was then calculated by solid geometry. This shape factor proved to be practically the same for all the sizes studied.

The Integral Method, outlined next, was basically the method reported by Bujac and Mullin (1969). It was much faster than the Differential Method, but in the case of growth, it could only be used at low supersaturations, where nucleation was completely absent. In the present work, the Integral Method was applied only to the growth of 1-mm crystals at 40°C.

When the temperature and initial concentration had been adjusted and the initial concentration found by specific gravity

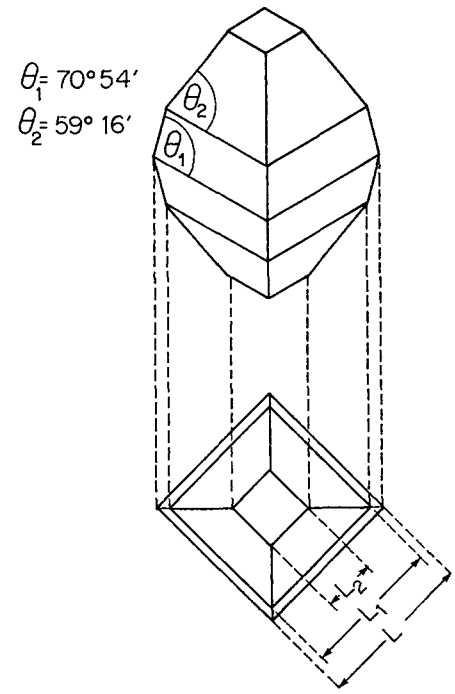

Fig. 3. Shape of nickel sulfate α-hexahydrate crystals.

bottle measurements, a large weight of seed crystals (several hundred grams) were charged. As with the Differential Method, the seed crystals were closely sized and preheated. The actual weight of seed crystals was so chosen that their percent size increase (calculated by mass balance from the planned fall-off of supersaturation) would be the same as that in the Differential Method, thereby maximizing the validity of comparisons between results at the same crystal size from the two methods. Once the weight of seed crystals had been chosen, the bed volume was reduced by the use of a false bottom (this was an annular Teflon constriction whose upper parts reproduced the shape of the glass reducer at the bottom of the crystallization section) to give an average calculated void fraction during the experiment of 0.80. This value is close to industrial levels.

As the seed crystals grew, the supersaturation fell by a large amount. This fall was continuously monitored by the specific gravity meter. When the supersaturation had fallen to the desired end value, the solution circulation was stopped and the bottle specific gravity samples for the final supersaturation were quickly taken. The output signal of the meter was linear with specific gravity between the two known end values. The product crystals were withdrawn and washed by the method previously described. Instantaneous rates of reduction of the supersaturation (calculated from a recorder trace of the meter output signal) were equated with instantaneous rates of growth on the seed crystals to give growth rates throughout the chosen range of supersaturation from a single experiment.

Full details of data handling for both Differential and Integral Methods are available elsewhere (Phillips, 1973).

CRYSTAL GROWTH RATES

The growth rates found by the Differential Method for different crystal sizes at 40°C and for different temperatures at a crystal size of 1.01 mm are plotted as functions of supersaturation in Figures 4 and 5, respectively. The rates are fully tabulated elsewhere (Phillips, 1973). Throughout this work, supersaturation is expressed as actual concentration minus saturation concentration, while concentrations are expressed as wt. % hexahydrate. All the growth rates measured in this work are strictly growth rates averaged over the different types of face

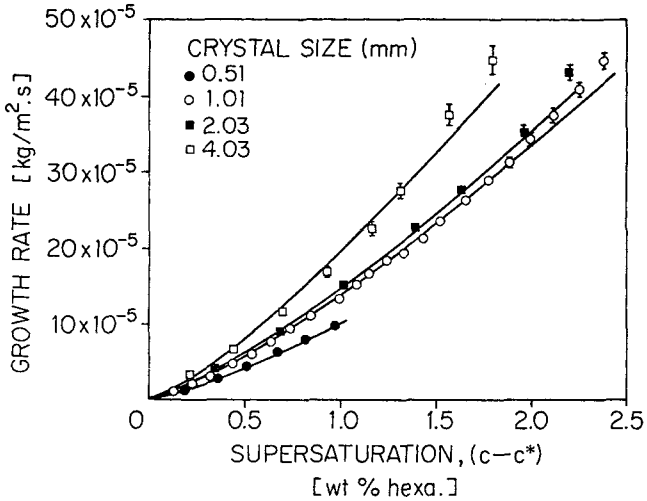

Fig. 4. Growth rates by Differential Method of different sized nickel sulfate α-hexahydrate crystals at 40°C. Bars show the 95% confidence limits when these extend beyond the point symbols.

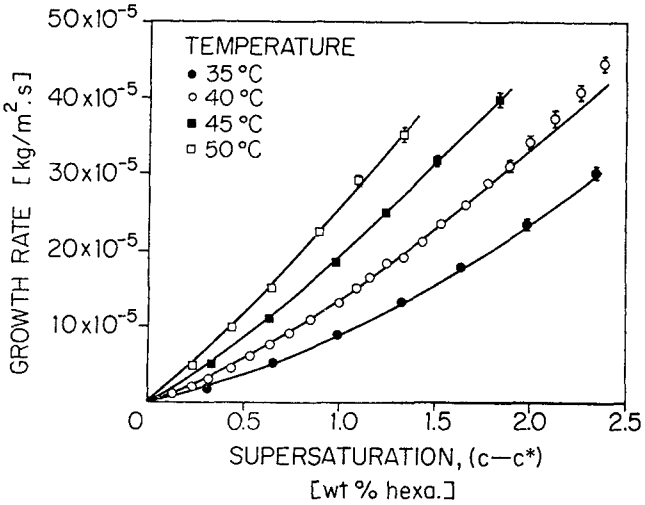

Fig. 5. Growth rates by Differential Method of 1.01 mm nickel sulfate α-hexahydrate crystals at different temperatures. Bars show the 95% confidence limits when these extend beyond the point symbols.

present on the crystal: actually, each type of face grows at a different rate, but these different rates on the different types of face cannot be separately determined solely from overall weight increases of the crystal. With nickel sulfate α-hexahydrate, there is evidence (Phillips, 1973) that in fact the differences in the growth rates on the different types of face are not great.

The estimated absolute standard error (estimated standard deviation of the sample mean) on the supersaturations was constant at 0.007 wt. % hexahydrate. The estimated percentage standard error on the growth rates was constant within each series of experiments at a given temperature and crystal size but was different for different series, ranging from 1.1% to 2.2%. Replicate experiments were made to estimate the standard error of the crystal weight change itself, but in most cases the major contribution to the standard error of the growth rates was from the standard error of the calculated overall surface-volume shape factor, due to the variations of L_1/L and L_2/L (Figure 3) between individual crystals.

In the present work, the Integral Method was applied only to growth and only at a temperature of 40°C and for a crystal size of 1.01 mm. In separate experiments, the supersaturation ranges 0.00 to 0.67 and 0.67 to 1.30 wt. % hexahydrate were covered, duplicate experiments being made for each range. The resulting curves of growth rate against supersaturation are shown in Figure 6. The estimated percentage standard error of the growth rates was 1.1%, the major contribution again being from the calculated overall surface-volume shape factor. For comparison, results from the Differential Method for 1.01-mm crystals at 40°C are also shown in Figure 6. The agreement is good over the range of supersaturation 0.00 to 0.67 wt. % hexahydrate, but over the range 0.67 to 1.30 wt. % hexahydrate, the results from the Integral Method are about 15% lower than those from the Differential Method. The reason for this difference is uncertain. Nucleation can be ruled out as a cause: hardly any nucleation was observed and, besides, nucleation would increase the rates of fall-off of supersaturation and hence apparently increase rather than decrease the growth rates. Another factor is that the true (interstitial) solution velocities past crystals of a given size are somewhat different in the two different methods because the interstitial solution velocity varies with the void fraction. In general, crystal growth rates vary with solution velocity (as discussed in more detail below), so the growth rates in a dense bed, with a smaller interstitial solution velocity, are expected to be somewhat lower than in a lean bed, with a larger interstitial solution velocity. However, if this were the cause of the observed differences in the results from the two methods, it would be expected to affect not one but both of the ranges of supersaturation used in the Integral Method.

Curves of the form

$$r = K \cdot (c - c^*)^N \qquad (1)$$

were fitted to the Differential Method growth rate measurements as follows. Logarithms were taken of both growth rates and supersaturations. In this form, the absolute estimated standard errors on the growth rates were constant within each series, so unweighted linear least squares fits were performed on these logarithmic values. In most cases these fits gave no statistically significant lack of fit. The slope of the linear fit directly gave N, together with its estimated standard error and the intercept of the linear fit gave log K together with the estimated standard error of log K. From these, K

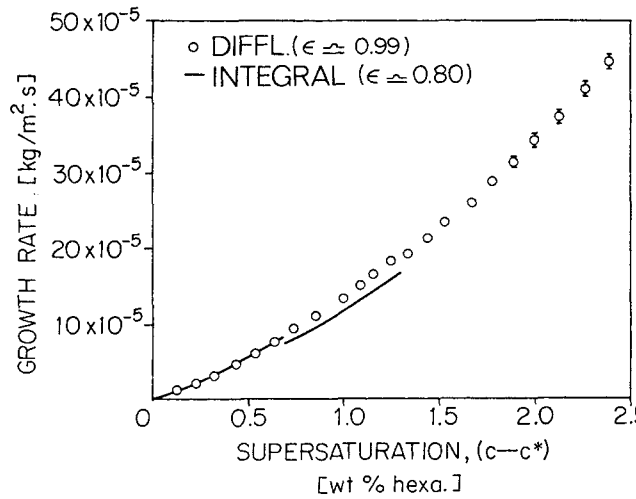

Fig. 6. Growth rates of 1.01 mm nickel sulfate α-hexahydrate crystals at 40°C by the Differential and Integral Methods. Bars show the 95% confidence limits when these extend beyond the point symbols.

Table 1. Best Fit Parameters of Equation (1) for Growth of Crystals of Different Sizes at 40°C

Mean crystal size, mm	K kg/m² · s · (wt. % hexa.)^N	Estimated absolute standard error of K	N dimensionless	Estimated absolute standard error of N
0.51	10.07×10^{-5}	0.11×10^{-5}	1.267	0.013
1.01	13.68×10^{-5}	0.11×10^{-5}	1.282	0.011
2.03	14.93×10^{-5}	0.26×10^{-5}	1.245	0.029
4.03	19.54×10^{-5}	0.61×10^{-5}	1.232	0.047

Table 2. Best Fit Parameters of Equation (1) for Growth of Crystals of Size 1.01 mm at Different Temperatures

Temperature, °C	K kg/m² · s · (wt. % hexa.)^N	Estimated absolute standard error of K	N dimensionless	Estimated absolute standard error of N
35.00	9.02×10^{-5}	0.05×10^{-5}	1.390	0.009
40.00	13.68×10^{-5}	0.11×10^{-5}	1.282	0.011
45.00	19.10×10^{-5}	0.07×10^{-5}	1.216	0.007
50.00	25.41×10^{-5}	0.17×10^{-5}	1.155	0.011

and the estimated standard error of K were calculated. These values of K and N are given in Tables 1 and 2, and the fitted lines are shown in Figures 4 and 5.

EFFECT OF SOLUTION VELOCITY AND CRYSTAL SIZE ON GROWTH RATE

It is generally believed that crystallization is a two-step process. Solute reaches the crystal surface, where, experimentally, the solution is still somewhat supersaturated, by normal mass transfer from the bulk solution. There is then supposed to be a surface integration process whereby solute species are incorporated into the solid lattice. Modern ideas about this latter step are discussed by Ohara and Reid (1973). In steady state growth, the two steps proceed at equal rates, usually expressed by

$$r = k_m (c - c_i) \tag{2}$$

$$r = k_r (c_i - c^*)^n \tag{3}$$

Equation (3) is in common use, but it is admittedly rather empirical. Equivalent equations predicted by theory are much more complicated (Ohara and Reid, 1973) and at present they cannot usefully be applied in analysing experimental data. Here, as elsewhere in the present work, concentrations are expressed as wt. % hexahydrate and growth rates as mass fluxes.

The mass transfer step is expected to be first order in concentration driving force $(c - c_i)$, as written here, but it is not necessarily true (although it is true in some cases) that the surface integration step is first order in $(c_i - c^*)$. In other words n is not necessarily unity. Nor is it necessarily an integer. The interfacial concentration c_i is difficult to measure, and direct determination of the constants k_m and k_r has not yet been achieved. Often, as has been the case so far in the present work, the growth rate can only be expressed in the more empirical form of Equation (1). As we have already seen in this study, N, like n, is neither necessarily unity nor even an integer. When growth is fully mass transfer controlled, that is, when k_r is much greater than k_m, then K tends to k_m and N tends to unity. On the other hand, when growth is fully surface controlled, that is, when k_m is much greater than k_r, then K tends to k_r and N tends to n.

Crystallization, then, is a process which in general involves a mass transfer step. If the growth mass transfer coefficient k_m were available, the separate contribution of mass transfer to the overall growth kinetics could be expressed in the usual way as

$$Sh \left(= \frac{k_m \cdot L}{\rho \cdot D} \right) = A \cdot (Re)^{\beta} \cdot (Sc)^{\alpha} \tag{4}$$

since, in this study, Sh is one or two orders of magnitude greater than unity, the range of crystal Reynolds number being 1.4 to 125. For the ranges of conditions usual in crystallization, solution density, diffusion coefficient, and kinematic viscosity are effectively constant, so that at constant temperature this expression can be reduced to

$$k_m \propto V^{\beta} \cdot L^{\beta - 1} \tag{5}$$

which gives the general dependence of the growth mass transfer coefficient on the velocity of the solution past the crystal and on the crystal size, at constant temperature. If we limit ourselves to fluidized beds, a further simplification is possible because V and L are then interrelated. In fact if the range of crystal size considered is not too large and if the void fraction is constant, then approximately

$$V \propto L^a \tag{6}$$

as is found from measurements of crystal fluidization velocities (Bujac, 1969; Mullin and Garside, 1970; Phillips, 1973). (Theoretically, for single spheres, $a = 2$ in the Stokes flow regime and $a = 0.5$ in the Newton flow regime.) Hence in fluidized beds

$$k_m \propto L^b \tag{7}$$

where

$$b = \beta(a + 1) - 1 \tag{8}$$

Thus in fluidized beds the growth mass transfer coefficient apparently depends on crystal size only although in fact part of this dependence on size is really dependence on solution velocity, as shown in Expression (5).

As we now recall, k_m itself is generally not available. Some workers have neglected the fact that K is not a true mass transfer coefficient and have expressed the apparent dependence of K itself on crystal size in the same form as Expression (7) to give

$$K \propto L^{b'} \tag{9}$$

Experimental values of b' for a few different kinds of crystals have been reported (Mullin and Garside, 1967). They are all within the range zero to one. The simplified Expression (9) is useful in crystallizer design (Bransom, 1960) but a more general expression, in which the effects of solution velocity and crystal size are not combined, is obtained by replacing k_m directly by K in Equation (4) to give

$$Sh' \left(= \frac{K \cdot L}{\rho \cdot D} \right) = A' \cdot (Re)^{\beta'} \cdot (Sc)^{\alpha'} \tag{10}$$

Mullin and Gaska (1969) found $\beta' = 0.87$ for potassium sulfate at 20°C.

When attempting to apply Expression (9) or Equation (10) in order to find the value of b' or of β', a problem arises if the value of N is different at different values of L. When this is so, the dimensions of K, kg/m² · s · (wt. % hexa)^N, are different for different values of L and it is

Table 3. Values of K for Different Crystal Sizes at 40°C when Growth Rate Curves Were Refitted Using $N = 1.257$ for All Crystal Sizes

Mean crystal size, mm	K kg/m² · s · (wt. % hexa.)$^{1.257}$
0.51	10.04×10^{-5}
1.01	14.14×10^{-5}
2.03	15.10×10^{-5}
4.03	20.22×10^{-5}

therefore of doubtful meaning to plot log K directly against log L. In the present work the differences in the values of N at different values of L (Table 1) were not statistically significant so that the arithmetic average value of N was found (1.257) and the growth rate curve-fits for different crystal sizes at 40°C were redetermined all with this fixed value of N. This gave the values of K shown in Table 3. These values were numerically close to the previous values of K (Table 1) but, unlike them, were all of the same dimensions, kg/m² · s · (wt. % hexa)$^{1.257}$, and thus their logarithms could be plotted against the logarithms of the values of L. When this was done, and a straight line fit made (not shown here), the resulting value of b' for nickel sulfate α-hexahydrate at 40°C was 0.31, with an estimated standard error of 0.05.

In order to present the direct dependences of K on solution velocity and on crystal size fully in the form of Equation (10), suitable diffusion coefficient data are needed so that the Schmidt number can be calculated. In the present case such data were not available: the only diffusion coefficient measurements for nickel sulfate solutions which could be traced were those by Oholm (1937), but these were at 20°C and for low concentrations, and extrapolation to other temperatures and concentrations is dangerous (Nienow, 1965). Nevertheless, the exponent β' can still be found by plotting log $(K \cdot L)$ against log $(V \cdot L)$ at constant temperature. When this was done, using the dimensionally consistent values of K from Table 3, and a straight line fit made (Figure 7), the resulting value of β' for nickel sulfate α-hexahydrate at 40°C was 0.61, with an estimated standard error of 0.03.

EFFECT OF TEMPERATURE ON GROWTH RATE

Many authors have tested the temperature dependence of experimental crystal growth rates against the Arrhenius relationship:

$$\text{rate constant} \propto \exp\left[-E/(R \cdot T)\right] \qquad (11)$$

However, modern theories of the surface process predict a complicated dependence of growth rate on temperature (Ohara and Reid, 1973). Thus, except in the case of full mass transfer control of the growth rate, the E term in Expression (11) has little physical significance, and the Arrhenius form is useful only as an empirical relation between growth rate and temperature. In general then, when analyzing the dependence of experimental growth rates on temperature, one can at present do little beyond noting that the growth rate increases as temperature increases.

CRYSTAL DISSOLUTION RATES

The dissolution rates found by the Differential Method for different crystal sizes at 40°C and for different temperatures at a crystal size of 1.00 mm are plotted as functions of undersaturation in Figures 8 and 9, respectively. The rates are fully tabulated elsewhere (Phillips, 1973). The estimated standard errors on the undersaturations and dissolution rates are the same as for the supersaturations and growth rates, respectively.

The dissolution rate measurements were first fitted by least squares straight lines constrained to pass through the origin. As their percent error, rather than their absolute error, was constant, the measurements were weighted accordingly. However, in all cases these constrained lines gave a statistically significant lack of fit, so instead, unconstrained straight lines were used, again with weighting. These latter lines are shown in Figures 8 and 9. In most cases they gave no statistically significant lack of fit. The meaning of the small, but significant, positive intercepts on the undersaturation axis is not

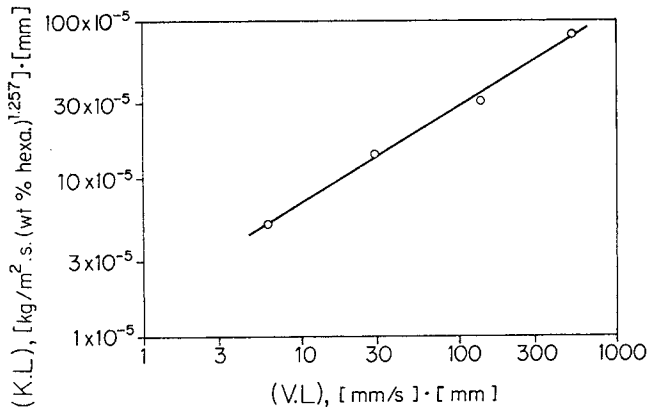

Fig. 7. Pseudo-mass transfer correlation of overall growth rate constant K with interstitial solution velocity V and crystal size L at 40°C.

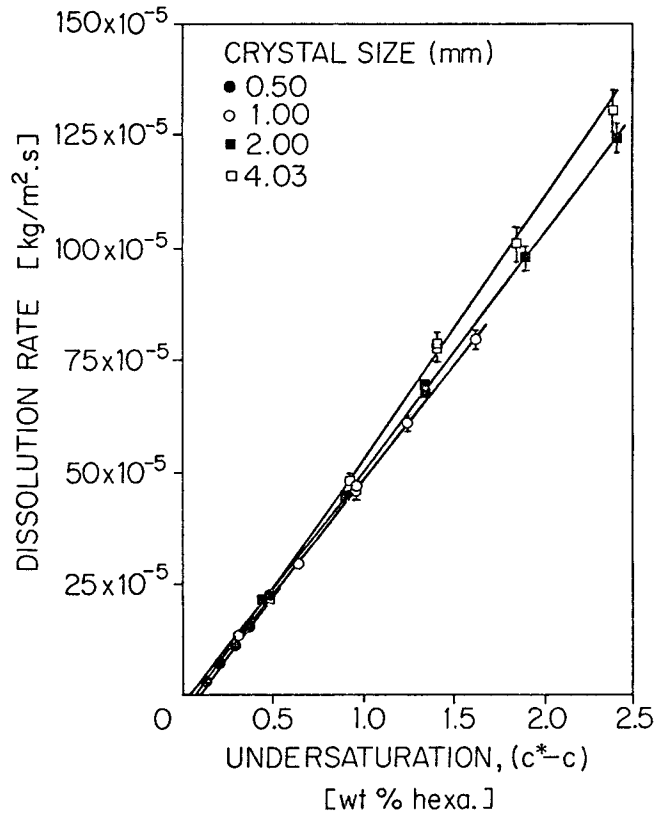

Fig. 8. Dissolution rates by Differential Method of different sized nickel sulfate α-hexahydrate crystals at 40°C. Bars show the 95% confidence limits when these extend beyond the point symbols.

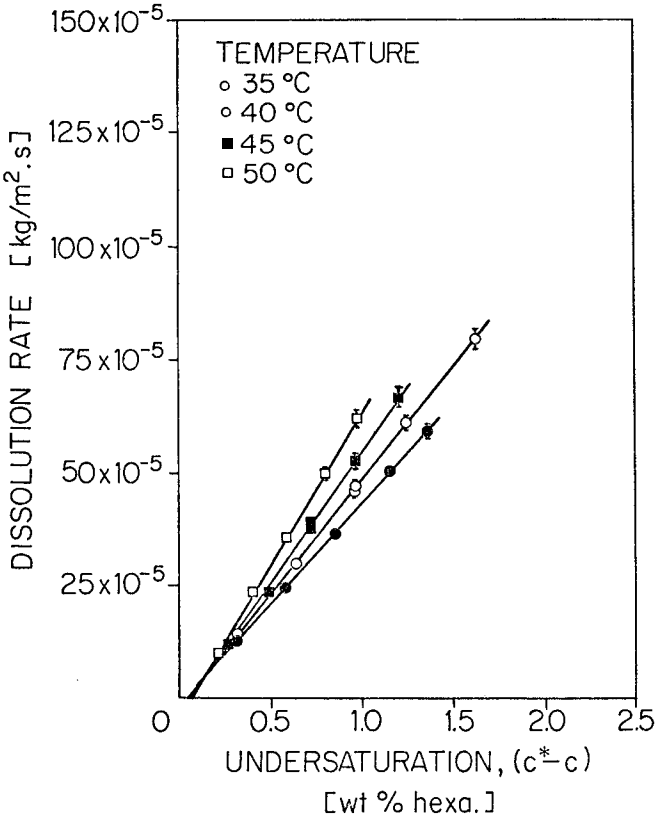

Fig. 9. Dissolution rates by Differential Method of 1.00 mm nickel sulfate α-hexahydrate crystals at different temperatures. Bars show the 95% confidence limits when these extend beyond the point symbols.

certain. Possibly the actual saturation concentration had fallen below the expected value because of a buildup of impurities. In the case of growth, such intercepts have been observed by other workers (for example, Rumford and Bain, 1960; Mullin and Gaska, 1969) but in the present work they were observed only in the case of dissolution. Cooke (1960) has reported that with sodium chloride intercepts exist for both growth and dissolution. The dissolution rate constants k_d in the equations

$$r_d = k_d \cdot (c^* - c) \qquad (12)$$

were taken as the slopes of the unconstrained lines, ignoring the intercepts. These constants and their estimated standard errors are given in Tables 4 and 5.

In this work, as is usual, dissolution appeared to be purely a mass transfer process so the dependence of k_d on crystal size and solution velocity can be expressed directly in the form of Equation (4). As outlined above, an absolute comparison with published fluidized bed mass transfer correlations could not be made here because of a lack of diffusion coefficient data, but a plot of log $(k_d \cdot L)$ against log $(V \cdot L)$ at constant temperature (Figure 10) yielded $\beta = 0.49$ (with estimated standard error 0.03), a value close to those given by Rowe and Claxton (1965) for spheres at similar Reynolds numbers. For the dissolution of potassium alum, Mullin and Garside (1968) found $\beta = 0.62$. For the dependence of k_d on temperature, an Arrhenius plot for 1.00 mm crystals gave a good straight line (not shown here) leading to an activation energy of 23 kJ/mol (5.5 kcal/mol), which is of the order expected for processes occurring by physical mechanisms.

Table 4. Best Fit Values of k_d from Equation (12) for Dissolution of Crystals of Different Sizes at 40°C

Mean crystal size, mm	k_d kg/m² · s · (wt. % hexa.)	Estimated absolute standard error of k_d
0.50	51.33×10^{-5}	1.47×10^{-5}
1.00	50.62×10^{-5}	0.35×10^{-5}
2.00	52.52×10^{-5}	0.34×10^{-5}
4.03	58.57×10^{-5}	0.83×10^{-5}

Table 5. Best Fit Values of k_d from Equation (12) for Dissolution of Crystals of Size 1.00 mm at Different Temperatures

Temperature, °C	k_d kg/m² · s · (wt. % hexa.)	Estimated absolute standard error of k_d
35.00	43.96×10^{-5}	0.17×10^{-5}
40.00	50.62×10^{-5}	0.35×10^{-5}
45.00	57.22×10^{-5}	1.37×10^{-5}
50.00	66.97×10^{-5}	0.70×10^{-5}

APPARENT SURFACE INTEGRATION KINETICS

In this work, both growth and dissolution rates have been found under hydrodynamic conditions deliberately made as similar as possible in the two cases. In the following extraction of the apparent kinetics of the surface integration step of growth [Equation (3)] from the overall kinetics of growth [Equation (1)], it is assumed that the mass transfer step of growth can be represented by dissolution rate expressions; in other words, that under given conditions k_m equals k_d. Before proceeding, it is emphasized that although it has been used by several workers, this assumption is open to dispute. Illustrating this point, Mullin and Garside (1968) write: "During growth, solute molecules are diffusing towards the crystal surface, whilst during dissolution they are travelling in the opposite direction. It is possible that electrostatic charges attracting solute molecules to the crystal surface would increase the rate of diffusion in the former case but decrease the rate in the latter." Indeed, the values of k_m which they themselves calculated by estimating k_r from measurements of the limiting growth rate at high solution velocities are considerably greater than the values of k_d for similar conditions, and the same kind of discrepancy was found by Clontz et al. (1972). However, the values of k_m found by Rumford and Bain (1960) from mass transfer controlled growth were in good agreement with values of

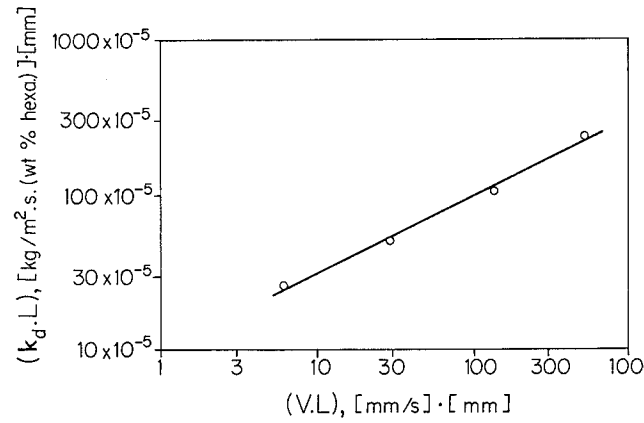

Fig. 10. Mass transfer correlation of dissolution rate constant k_d with solution velocity V and crystal size L at 40°C. The 95% confidence limits are all within the point symbols.

k_d calculated from the mass transfer correlation of Chu et al. (1953).

Having made the assumption discussed above, we substitute $k_m = k_d$ in Equation (2) and hence calculate

$$r/k_m = (c - c_i) \tag{13}$$

Then

$$(c - c^*) - (r/k_m) = (c - c^*) - (c - c_i) = (c_i - c^*) \tag{14}$$

Plots of r against $(c_i - c^*)$ thus computed are shown in Figures 11 and 12. Logarithmic curve-fits then yielded the apparent values of k_r and n (Tables 6 and 7). The exponent n is expected to be independent of crystal size, and the present values of n at different crystal sizes are indeed not significantly different. The rate constant k_r might also be expected to be independent of the hydrodynamics and thus of crystal size. However, as yet there is no convincing experimental verification of this prediction by the present method. Certainly in this work the values of k_r retain a dependence on crystal size (Table 6), and despite their smaller range of crystal size and larger standard error of k_r, Mullin and Garside (1968) similarly report some dependence of k_r on crystal size.

There is some prior experimental evidence both for and against the idea that k_r varies with crystal size. For example, at high solution velocities, when the growth rate was almost independent of solution velocity, McCabe and Stevens (1951) and Rosen and Hulburt (1971) found the growth rate to be independent of crystal size as well. Mullin and Gaska (1969) found that their crystal growth rates varies with crystal size. This fact, together with the fact that the activation energy for growth was low, led them to conclude that growth of potassium sulfate was diffusion controlled. However, they found $N = 2$ for all crystal sizes, whereas for diffusion control $N = 1$ would be expected. Another interpretation of their data is that, since $N = 2$ for all crystal sizes, surface integration at least partly controls the growth rate and the surface integration rate is size-dependent. Bujac (1969) has concluded from his experimental observations that the surface integration rate does depend on the hydrodynamics, and he therefore considers the simple diffusion theory of growth of the type used in the present work to be inadequate.

Of several theoretical models of the surface process, one, the mono-nuclear two-dimensional nucleation model, does predict a dependence of surface-controlled growth rate on crystal size (Ohara and Reid, 1973). However, this model is usually considered to be unrealistic. It is conceivable that some property of the surface (such as dislocation density) which may influence the surface integration rate, may change during the growth of batches of seed crystals to their different intended sizes, thereby causing seed crystals of different sizes to have different surface properties and hence causing a variation of the surface integration rate with crystal size.

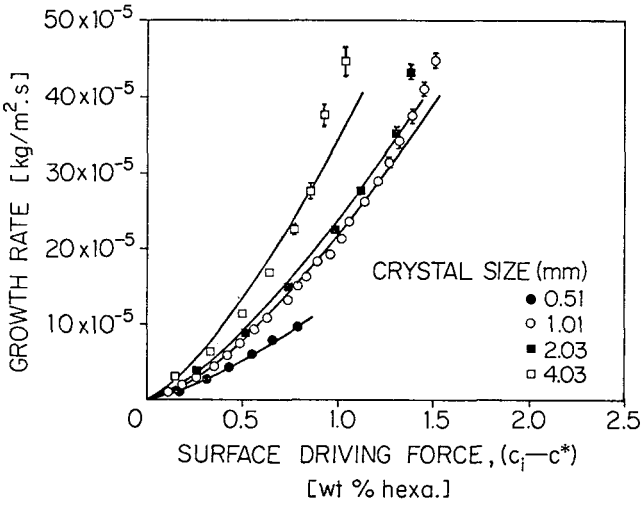

Fig. 11. Apparent surface integration rates of different sized nickel sulfate α-hexahydrate crystals at 40°C. Bars show the 95% confidence limits when these extend beyond the point symbols.

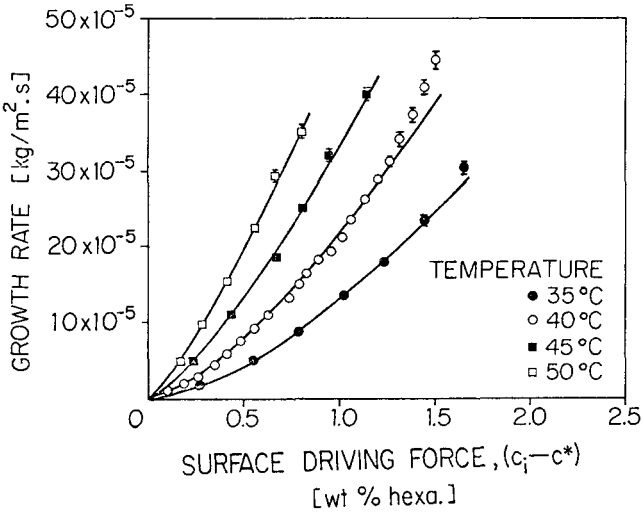

Fig. 12. Apparent surface integration rates of 1.01 mm nickel sulfate α-hexahydrate crystals at different temperatures. Bars show the 95% confidence limits when these extend beyond the point symbols.

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TABLE 6. BEST FIT PARAMETERS OF EQUATION (3) FOR GROWTH OF CRYSTALS OF DIFFERENT SIZES AT 40°C

Mean crystal size, mm	k_r kg/m² · s · (wt. % hexa.)^n	Estimated absolute standard error of k_r	n dimensionless	Estimated absolute standard error of n
0.51	13.43×10^{-5}	0.24×10^{-5}	1.349	0.020
1.01	21.78×10^{-5}	0.35×10^{-5}	1.426	0.021
2.03	23.82×10^{-5}	0.76×10^{-5}	1.371	0.059
4.03	34.36×10^{-5}	2.70×10^{-5}	1.351	0.097

TABLE 7. BEST FIT PARAMETERS OF EQUATION (3) FOR GROWTH OF CRYSTALS OF SIZE 1.01 MM AT DIFFERENT TEMPERATURES

Temperature, °C	k_r kg/m² · s · (wt. % hexa.)^n	Estimated absolute standard error of k_r	n dimensionless	Estimated absolute standard error of n
35.00	13.00×10^{-5}	0.18×10^{-5}	1.544	0.025
40.00	21.78×10^{-5}	0.35×10^{-5}	1.426	0.021
45.00	33.11×10^{-5}	0.50×10^{-5}	1.342	0.023
50.00	46.67×10^{-5}	0.56×10^{-5}	1.269	0.015

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NOTATION

a = exponent of L in Expression (6), dimensionless
A = constant in Equation (4), dimensionless
A' = constant in Equation (10), dimensions depend on those of K
b = exponent of L in Expression (7), dimensionless
b' = exponent of L in Expression (9), dimensionless
c = concentration of bulk solution, supersaturated in the case of growth, undersaturated in the case of dissolution, wt. % hexahydrate
c^* = saturation concentration, wt. % hexahydrate
c_i = in the case of growth, the (supersaturated) solution concentration at the crystal surface, wt. % hexahydrate
D = diffusion coefficient, m^2/s
E = activation energy; used in Expression (11), kJ/mol
k_d = dissolution mass transfer coefficient; defined by Equation (12), $kg/m^2 \cdot s \cdot$ (wt. % hexa.)
k_m = growth mass transfer coefficient; defined by Equation (2), $kg/m^2 \cdot s \cdot$ (wt. % hexa.)
k_r = surface integration rate constant; defined by Equation (3), $kg/m^2 \cdot s \cdot$ (wt. % hexa.)^n
K = overall growth rate constant; defined by Equation (1), $kg/m^2 \cdot s \cdot$ (wt. % hexa.)^N
L = crystal size, mm or m
n = exponent of $(c_i - c^*)$ in Equation (3), dimensionless
N = exponent of $(c - c^*)$ in Equation (1), dimensionless
r = growth rate, $kg/m^2 \cdot s$
r_d = dissolution rate, $kg/m^2 \cdot s$
R = gas constant, = 8.31 J/mol · kelvin
T = in Expression (11), absolute temperature, K
V = interstitial solution velocity = true velocity of solution past crystals, mm/s or m/s

Re = Reynolds number $= \dfrac{V \cdot L}{\nu}$

Sc = Schmidt number $= \dfrac{\nu}{D}$

Sh = Sherwood number $= \dfrac{k_m \cdot L}{\rho \cdot D}$ or $\dfrac{k_d \cdot L}{\rho \cdot D}$

Sh' = Pseudo-Sherwood number $= \dfrac{K \cdot L}{\rho \cdot D}$

Greek Letters

α = exponent of Schmidt number in Equation (4), dimensionless
α' = exponent of Schmidt number in Equation (10), dimensionless
β = exponent of Reynolds number in Equation (4), dimensionless
β' = exponent of Reynolds number in Equation (10), dimensionless
ν = kinematic viscosity of the solution, m^2/s
ρ = density of the solution, kg/m^3

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